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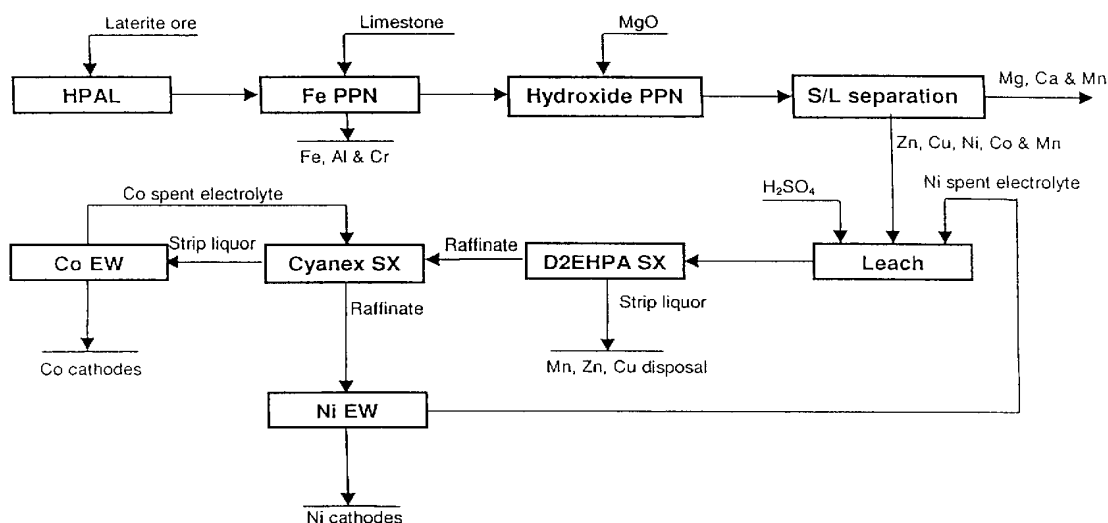
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(54) Title: RECOVERY OF NICKEL AND COBALT FROM LEACH SOLUTIONS



(57) Abstract: A method of separating cobalt and nickel from other elements contained in an aqueous leach solution, the method including the steps of: adding a precipitating agent to the aqueous leach solution to precipitate elements including cobalt and nickel; separating the precipitate from the treated aqueous leach solution; leaching the precipitate with an acid to form a leach liquor; and subjecting the leach liquor to successive solvent extraction steps with an organophosphoric acid and an organophosphinic acid.



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RECOVERY OF NICKEL AND COBALT FROM LEACH SOLUTIONS

The present invention relates to a method of separating cobalt and nickel from other elements contained  
5 in an aqueous leach solution.

The world mineral industry is experiencing an unprecedented interest in nickel-cobalt extraction from laterite ores through high pressure acid leach (HPAL) and  
10 solvent extraction - electrowinning (SX-EW) processes. In WA, three nickel laterite projects have been commissioned. These are the Cawse project of Centaur Mining Ltd, the Bulong project of Preston Resources and the Murrin Murrin project of Anaconda Nickel Ltd. The HPAL process for the  
15 three projects is very similar, however the down stream processes (including SX) differ substantially.

In the Murrin Murrin process (Motteram et al., 1996), a sulfide precipitation is used to separate the  
20 nickel, cobalt, copper and zinc from impurities such as calcium, magnesium and manganese which remain in the leach solution. After solids/liquid separation, the nickel, cobalt, copper and zinc are re-leached under pressure with acid. Further solution purification is needed to separate  
25 nickel and cobalt from copper and zinc. The cobalt is then separated from nickel by solvent extraction with Cyanex 272. The nickel and cobalt are recovered by reduction with hydrogen. The drawbacks of the Murrin Murrin process are:

- 30 • The separation of manganese from cobalt by sulphide precipitation is incomplete and causes problems in the downstream processes,
- The leaching of sulphides needs high pressure and high temperature, indicating high capital and operating  
35 costs.
- The separation of other impurities such as copper and zinc from nickel and cobalt needs separate processes.

In the Cawse process (Manson et al., 1997), a hydroxide precipitation is used to separate the impurities such as calcium, magnesium and manganese (partly). After solids/liquid separation, the nickel, cobalt, copper and zinc are re-leached with an ammoniacal solution. Nickel and copper are separated from cobalt and zinc by solvent extraction with LIX84I. Further solution purification is needed to separate nickel from copper and cobalt from zinc. The nickel is recovered by electrowinning while cobalt is precipitated as sulphide. The drawbacks of the Cawse process are:

- The use of ammoniacal leaching to separate manganese from cobalt results in complexity of the flowsheet and causes serious problems in the downstream processes,
- The reductive stripping of cobalt from organic extractant and the re-oxidation of the organic extractant cause organic degradation (Kindred, 2000), which in turn results in crud formation,
- Ammonia is expensive and the scrubbing and recovery of ammonia are difficult,
- Cobalt product containing zinc is a semi-product, indicating revenue loss.

The Bulong process (Taylor and Cairns, 1997), uses a direct solvent extraction approach. Cobalt, copper, zinc and manganese are separated from nickel, calcium and magnesium by solvent extraction with Cyanex 272. The nickel in the raffinate is separated from calcium and magnesium by solvent extraction with Versatic 10 and then electrowon. The solution containing cobalt, copper, zinc and manganese is subjected to sulphide precipitation, solids/liquid separation and acid pressure re-leach to separate cobalt, copper and zinc from manganese. The copper is eliminated from the solution by ion exchange and zinc by solvent extraction with D2EHPA. The cobalt is then recovered from

the purified solution by electrowinning. The drawbacks of the Bulong process are:

- Manganese is separated from cobalt by sulphide precipitation and other impurities are separated by different further processes (ion exchange and further SX),
- Gypsum precipitation occurs in both Cyanex 272 and Versatic 10 circuits,
- Aqueous feed solution with its original volume is treated twice - in both the Cyanex and Versatic 10 SX circuits. This requires larger circuits (higher capital expenditure) than if the valuable metal (nickel) were concentrated by extraction into the organic phase in the first circuit.

An object of the present invention is to provide a practical process for separating cobalt and nickel from impurities contained in leach solutions such as those derived from lateritic ores.

Accordingly, the present invention provides a method of separating cobalt and nickel from other elements contained in an aqueous leach solution, the method including the steps of:

- (a) adding a precipitating agent to the aqueous leach solution to precipitate elements including cobalt and nickel;
- (b) separating the precipitate from the treated aqueous leach solution;
- (c) leaching the precipitate with an acid to form a leach liquor; and
- (d) subjecting the leach liquor to successive solvent extraction steps with an organophosphoric acid and an organophosphinic acid.

As will be understood to persons skilled in the

art of the invention, the aqueous leach solution may be the leach solution obtained from acid digestion of an ore or ore concentrate, or may be a leach solution that has been subjected to other procedures to remove undesired elements therefrom. For instance, the leach solution may be one that has been subjected to a preliminary iron precipitation step.

The precipitating step is intended to precipitate out the cobalt and nickel (and some other elements) as a salt at the given pH, which precipitates can be re-leached in an acid. The pH will be one at which other elements (cations) in the aqueous leach liquor are not precipitated. Any precipitating agent that would effect precipitation of the cobalt and nickel as an appropriate salt at the given pH would be appropriate. The precipitate is preferably a hydroxide or a carbonate, however other salts such as oxylate salts could be envisaged. If the precipitate is a hydroxide or carbonate, suitable precipitating agents would include alkaline earth metal oxides (magnesia, calcium oxide etc) alkaline earth metal carbonates (magnesium carbonate, calcium carbonate) alkali oxides and alkali carbonates. Magnesia is the preferred precipitating agent. The elements that are precipitated out as hydroxides or carbonates will include zinc, copper, nickel and cobalt, to the extent that these elements are present in the aqueous leach solution. Some manganese may also be precipitated.

Any suitable acid may be used to re-leach the precipitate, such as sulphuric acid, hydrochloric acid, nitric acid and so on. Sulphuric acid is preferred.

The precipitation step effects the removal of magnesium and calcium (to the extent that these elements are present in the aqueous leach solution), and some manganese, which elements remain in the aqueous leach solution.

If the leach liquor (ie the liquor obtained following the re-leaching step) is subjected to solvent extraction with organophosphoric acid first, the aqueous raffinate from the organophosphoric acid leaching stage is subjected to solvent extraction with the organophosphinic acid. Nickel may recovered from the raffinate by any suitable technique, such as electrowinning, and cobalt recovered from the aqueous strip liquor by any suitable technique, such as electrowinning.

If the leach liquor is subjected to solvent extraction with organophosphinic acid first, nickel is recovered from the raffinate of the organophosphinic acid extraction stage (eg by electrowinning), and the aqueous strip liquor from the organophosphinic acid extraction stage is subjected to solvent extraction with organophosphoric acid to produce a raffinate from which cobalt may be recovered, for example by precipitation. In the case of precipitation of the cobalt from the raffinate, this may be done by the addition of sodium hydroxide which will effect precipitation of the cobalt as cobalt hydroxide.

The loaded organic phase resulting from solvent extraction with organophosphoric acid may be scrubbed with an aqueous scrub solution containing manganese and copper. This aqueous scrub solution is preferably obtained by conducting a selective strip on a scrubbed loaded organic solution produced in the scrubbing step, and recycling the manganese and copper containing aqueous solution back to the scrubbing stage to be used as the aqueous scrub solution. A spent aqueous scrub solution generated in the scrubbing step is then recycled to the leach solution to maximise the recovery of cobalt (and nickel). The selectively stripped organic solution would usually then be subjected to bulk shipping to remove a large proportion of

the cations remaining therein to be recycled for use as the organic phase in the initial extraction step.

When the organophosphoric acid extraction step is conducted prior to the organophosphinic acid extraction step, preferably the organophosphoric acid extraction step involves:

- I. contacting the leach liquor produced in step (c) with an organic solution comprising an organophosphoric acid and a modifier dissolved in an organic solvent to produce a loaded organic solution containing manganese and, to the extent that they are present, zinc and copper, and a some cobalt and nickel, and an aqueous raffinate solution containing most of the cobalt and nickel;
- II. scrubbing the loaded organic solution with an aqueous scrub solution containing manganese and copper to produce a scrubbed organic solution containing less cobalt and nickel and a spent aqueous scrub solution containing some cobalt and nickel, as well as manganese;
- III. recycling the spent aqueous scrub solution to step I; and
- IV. selectively stripping the scrubbed organic solution to remove a portion of the manganese and copper to form the aqueous scrub solution for use in step II.

When the organophosphoric acid extraction step is conducted following the organophosphinic acid extraction step, preferably the organophosphoric acid extraction step involves:

- I. contacting the aqueous strip liquor from the organophosphinic acid extraction stage with an organic solution comprising an organophosphoric acid and a modifier dissolved in an organic solvent to produce a loaded organic solution containing manganese and, to the extent that they are present, zinc and copper, and

- a some cobalt, and an aqueous raffinate solution containing most of the cobalt;
- II. scrubbing the loaded organic solution with an aqueous scrub solution containing manganese and copper to
- 5 produce a scrubbed organic solution containing less cobalt and a spent aqueous scrub solution containing some cobalt, as well as manganese;
- III. recycling the spent aqueous scrub solution to step I; and
- 10 IV. selectively stripping the scrubbed organic solution to remove a portion of the manganese and copper to form the aqueous scrub solution for use in step II.

Preferably, the organophosphoric acid solvent

15 extraction step also includes the step of:

- V. bulk stripping the selectively stripped organic solution from step IV to remove a large proportion or almost all of the cations therein to regenerate the organic solution for recycling to step I.

20

In the most preferred embodiment of the invention, the organophosphoric acid is di-2-ethylhexyl phosphoric acid (D2EHPA), however it will be appreciated by persons skilled in the art that an organophosphoric acid

25 having extraction characteristics similar to D2EHPA could be used. Organophosphoric acids have the formula  $(RO)_2PO_2H$ , in which R represents an organic group. The two organic groups R, which may be the same or different, can be selected from optionally substituted branched, straight

30 chained or cyclic alkyl, alkenyl or alkynyl groups. Preferably the organic groups are fairly bulky, and have a minimum of 4 carbon atoms, more preferably from 6 to 18 carbon atoms. The organic groups may suitably be n-octyl, cyclooctyl or 2-ethylhexyl.

35

The modifier is any suitable modifier that improves separation of the organic and aqueous phases.



Suitable modifiers include 2-ethylhexanol, isodecanol and isotridecanol and tri n-butyl phosphate (TBP). TBP is the preferred modifier.

5           The organic solvent may be any suitable organic solvent for the organophosphoric acid that achieves good phase separation from the aqueous phase with the modifier. Kerosene is the most common solvent/diluent used for this purpose due to its low cost and availability.

10

          The scrubbed organic solution may be selectively stripped of manganese and copper by contacting it with an acid. Sulphuric acid is preferred due to its low cost, however other acids such as HCl and HNO<sub>3</sub> could be used.

15       The selectively stripped organic solution may be bulk stripped of impurity elements by contacting the selectively stripped organic solution with a second acid. The second acid should be stronger than the first acid, and may therefore be the same acid at a higher concentration, or a  
20       stronger acid. Accordingly, when sulphuric acid is used as the first acid, a more concentrated sulphuric acid or hydrochloric acid may be used as the second acid to bulk strip the selectively stripped organic solution of the impurity elements. The bulk stripped organic solution may  
25       then be recycled to step I.

          The range of the Mn and Cu in the aqueous scrub solution will depend on how much Co (and Ni) is to be scrubbed and the aqueous to organic (A/O) ratio.

30       Preferably, the mole ratio of (Mn+Cu)/(Co+Ni) is at least 1.5 for complete scrubbing.

          The amount of organophosphoric acid in the organic solution used in step I will depend on the  
35       concentration of the elements to be extracted and the A/O ratio, however the amount would typically be in the range of from 3% to 35% v/v, with a preferred range of 5% to 25%.

At levels above 35% the organic solution will be too viscous resulting in lower extraction kinetics.

5 The amount of modifier in the organic solution used in step I will also vary. The range of modifier will typically be in the range of 3% to 15% v/v, with a preferred range of 5% to 10%.

10 Preferably, the pH of the aqueous phase is maintained in a range from 3.0 to 4.5 and more preferably 3.5 to 4.0 in step I of the organophosphoric acid extraction stage. The temperature is preferably maintained in the range of from 10°C to 60°C, more preferably from 20 to 40°C. Whilst temperatures as low as 10°C are  
15 achievable, a temperature lower than 15°C results in high viscosity. At temperatures higher than 60°C there is a risk of evaporation and degradation of the organic phase.

20 The aqueous to organic ratio (A/O) in step I is most preferably 1:1, but may lie in the range from 10:1 to 1:10, and preferably 1:2 to 5:1. The aqueous to organic ratio maintained in step II may lie within the range of from 1:5 to 1:200, but preferably it is in the range of 1:5 to 1:20, and most suitably it is from 1:5 to 1:10.

25

In the most preferred embodiment of the invention, the organophosphinic acid is di-2,4,4-trimethylpentyl phosphinic acid (eg Cyanex 272). However it will be appreciated by persons skilled in the art that any organophosphinic acid having extraction characteristics similar to or the same as di-2,4,4-trimethylpentyl phosphinic acid could be used.  
30 Organophosphinic acids have the formula  $R_2PO_2H$ , in which R represents an organic group. The two organic groups R, which may be the same or different, can be selected from optionally substituted branched, straight chained or cyclic  
35 alkyl, alkenyl or alkynyl groups. Preferably the organic

groups are fairly bulky, and have a minimum of 4 carbon atoms, more preferably from 6 to 18 carbon atoms. The organic groups are preferably unsubstituted branched, straight chained or cyclic alkyl groups, and may suitably  
5 be n-octyl, cyclooctyl, 2-ethylhexyl or 2,4,4-trimethylpentyl.

The term "alkyl" used either alone or in a compound word such as "optionally substituted alkyl" or  
10 "optionally substituted cycloalkyl" denotes straight chain, branched or mono- or poly- cyclic alkyl, preferably C1-30 alkyl or cycloalkyl. Examples of straight chain and branched alkyl include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, amyl, isoamyl, sec-  
15 amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, heptyl, 5-  
20 methylhexyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, nonyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-methyloctyl, 1-, 2-, 3-, 4- or 5-ethylheptyl, 1-2- or 3-  
25 propylhexyl, decyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- and 8-methylnonyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3- or 4-propylheptyl, undecyl 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-methyldecyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-ethylnonyl, 1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl,  
30 1-pentylhexyl, dodecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-methylundecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-ethyldecyl, 1-, 2-, 3-, 4-, 5- or 6-propylnonyl, 1-, 2-, 3- or 4-butyloctyl, 1-2-pentylheptyl and the like. Examples of cyclic alkyl include cyclopropyl, cyclobutyl,  
35 cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl and cyclodecyl and the like. The alkyl may optionally be substituted by any non-deleterious

substituent.

In this specification "optionally substituted" means that a group may or may not be further substituted with one or more groups selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, benzylthio, acylthio and the like.

Suitable optional substituents will be chosen on the basis that the organophosphinic or organophosphoric acid have the desired extraction characteristics, and the substituents do not react with any other component of the mixture under the given extraction conditions.

The term "halogen" denotes fluorine, chlorine, bromine or iodine.

The amount of organophosphinic acid in the organic solution used in the organophosphinic acid solvent extraction step will depend on the concentration of the elements to be extracted and the A/O ratio, however the amount would typically be in the range of from 3% to 35% v/v, with a preferred range of 5% to 25%. At levels above 35% the organic solution will be too viscous resulting in lower extraction kinetics.

It is also advantageous to use a modifier in the

organophosphinic acid extraction stage as for the organophosphoric acid extraction stage. Again, TBP is preferred.

5                    Preferably, the pH of the aqueous phase is maintained in a range from 5.0 to 6.0 in the organophosphinic acid solvent extraction circuit. The temperature is preferably maintained in the range of from 10°C to 60°C, more preferably from 20 to 40°C. Whilst  
10 temperatures as low as 10°C are achievable, a temperature lower than 15°C results in high viscosity. At temperatures higher than 60°C there is a risk of evaporation and degradation of the organic phase.

15                    The aqueous to organic ratio (A/O) in the organophosphinic acid solvent extraction circuit is most preferably 1:1, but may lie in the range from 3:1 to 1:3.

                    The cobalt extracted into the loaded organic  
20 phase in the organophosphinic acid extraction circuit is stripped therefrom and either recovered (when following the organophosphoric acid extraction stage) or directed to the organophosphoric acid extraction stage. In the stripping stage, the A/O ratio may be from 1:2 up to 1:200, and the  
25 pH from 2.0 to 4.0. Other details concerning the organophosphinic acid extraction stage are well within the knowledge and experience of persons in the art of the invention.

30                    The steps outlined above can be conducted in combination with other solvent extraction steps and optionally one or more precipitation steps to separate certain elements from each other. For instance, it is common in the art of the invention for a preliminary iron  
35 precipitation step to be conducted to precipitate out iron to leave an aqueous leach solution containing the target elements. However, it is a major advantage of the process

of the present invention that no precipitation steps for the purpose of separating manganese from cobalt are required. Therefore, in a preferred embodiment of the invention, the process does not include a sulphide  
5 precipitation stage for separating cobalt from manganese.

It will be well understood to persons skilled in the art of the invention that scrubbing stages of the type well known in the art may be used for recovering elements  
10 even if the scrubbing stages are not specifically mentioned. The design of the optimum arrangement of scrubbing stages will depend on the specific aqueous leach solution and the elements desired to be recovered therefrom (and target percentage recovery levels).

15

The present invention also provides a plant for conducting the methods and processes described above (in which the organophosphoric acid extraction stage precedes the organophosphinic acid extraction stage), the plant  
20 including:

- a hydroxide or carbonate precipitation tank in which the aqueous leach solution is contacted with a precipitating agent;
- a solid liquid separator (such as a thickener) in which  
25 the aqueous leach liquor following the precipitation step is separated from the precipitate;
- a re-leaching tank in which the precipitate is re-leached;
- an organophosphoric acid solvent extraction contactor in  
30 which the re-leached liquor is contacted with the organophosphoric acid-containing organic solution;
- a scrubbing contactor for scrubbing the loaded organic solution generated in solvent extraction contactor;
- a stripping contactor in which the scrubbed organic  
35 solution generated in the scrubbing contactor is subjected to selective stripping to generate the aqueous scrub solution for use in the scrubbing contactor;

## 14

- a scrubbed organic solution conduit for conducting the scrubbed organic solution to the stripping contactor;
- an aqueous scrub solution conduit for conducting the aqueous scrub solution from the stripping contactor to  
5 the scrubbing contactor;
- a spent aqueous scrub solution conduit for conducting the spent aqueous scrub solution from the scrubbing contactor to the solvent extraction contactor; and
- an organophosphinic acid solvent extraction circuit in  
10 which the aqueous raffinate solution generated in the organophosphoric acid solvent extraction contactor is extracted with an organophosphinic acid.

The present invention also provides a plant for  
15 conducting the methods and processes described above (in which the organophosphinic acid extraction stage precedes the organophosphoric acid extraction stage), the plant including:

- a hydroxide or carbonate precipitation tank in which the  
20 aqueous leach solution is contacted with a precipitating agent;
- a solid liquid separator (such as a thickener) in which the aqueous leach liquor following the precipitation step is separated from the precipitate;
- 25 - a re-leaching tank in which the precipitate is re-leached;
- an organophosphinic acid solvent extraction circuit in which the re-leached liquor generated in the re-leaching tank is extracted with an organophosphinic acid;
- 30 - an organophosphoric acid solvent extraction contactor in which the aqueous strip liquor from the organophosphinic acid solvent extraction circuit is contacted with the organophosphoric acid-containing organic solution;
- a scrubbing contactor for scrubbing the loaded organic  
35 solution generated in solvent extraction contactor;
- a stripping contactor in which the scrubbed organic solution generated in the scrubbing contactor is

subjected to selective stripping to generate the aqueous scrub solution for use in the scrubbing contactor;

- a scrubbed organic solution conduit for conducting the scrubbed organic solution to the stripping contactor;
- 5 - an aqueous scrub solution conduit for conducting the aqueous scrub solution from the stripping contactor to the scrubbing contactor; and
- a spent aqueous scrub solution conduit for conducting the spent aqueous scrub solution from the scrubbing
- 10 contactor to the solvent extraction contactor.

Preferably the plant further includes an organic solution recycle conduit for conducting the partially stripped scrubbed solution from the stripping contactor to

15 the organophosphoric acid solvent extraction contactor. More preferably, a bulk stripping contactor is located in this recycle conduit, in which the partially stripped scrubbed solution is stripped of remaining impurities before being conducted to the solvent extraction contactor.

20

As will be understood to persons skilled in the art of the invention, the solvent extraction contactor is preferably a countercurrent solvent extraction contactor. Similarly, further scrubbing stages and vessels may be

25 included in the plant.

The plants described above will also include the necessary conduits for passing the subject streams from one vessel, stage or circuit to the next. The organophosphinic acid solvent extraction circuit would include an

30 organophosphinic acid solvent extraction contactor (preferably countercurrent), and possibly one or more scrubbing contactors, together with the appropriate conduits for passing the various streams between the

35 vessels in the plant. The plants may also include a cobalt recovery stage, for instance a cobalt precipitation vessel or an electrolytic cell in which a cobalt electrowinning



process can be conducted. The arrangement of an appropriate plant including all of these elements is well within the skill of a person in the art of the invention now that the direction has been provided to conduct the process for recovering cobalt in the manner described above.

Some preferred embodiments of the invention are described in the accompanying examples and figures, in which:

Figure 1 illustrates a flow chart for the one stage in the processes of the preferred embodiments of the invention, and represents schematically a part of the plants of the preferred embodiments of the invention; Figure 2 illustrates a schematic flow chart for one embodiment of the process of the invention, and represents schematically a plant for this embodiment of the invention; and Figure 3 illustrates a schematic flow chart for a second embodiment of the process of the invention, and represents schematically a plant for this embodiment of the invention.

Flow sheets for two alternative embodiments of the invention are illustrated in Figures 2 and 3. In these two figures, the boxes referring to "D2EHPA SX" (di-2-ethylhexyl phosphoric acid solvent extraction) should be understood to be a short-hand reference to all of the steps outlined in Figure 1.

The organophosphoric acid extraction stage which is a feature of the two processes of the preferred embodiments of the invention is described in detail in Figure 1. An aqueous leach solution 1 (which may be the stream exiting the "leach" box (the re-leach tank) in Figure 2 or the strip liquor exiting the "cyanex SX" box - the organophosphinic solvent extraction stage - in Figure

3) is fed into a countercurrent solvent extraction contactor 2 in which the aqueous leach solution 1 is contacted with an organic extractant solution 3 comprising a solution of an organophosphoric acid (D2EHPA) and a modifier (TBP) in an organic solvent (kerosene). The aqueous raffinate 4 from the solvent extraction contains most of the cobalt (and nickel, if present in the aqueous leach solution 1) and, to the extent that it is present, a large proportion of the magnesium, from which the cobalt (and nickel) may be recovered. However, it is noted that if the organophosphinic acid solvent extraction stage is conducted prior to the organophosphoric acid extraction stage, as in the case of the Figure 3 process, nickel has already been separated from the aqueous leach solution, and the aqueous raffinate 4 from the organophosphoric extraction stage contains cobalt.

The loaded organic liquor 5 from the solvent extraction contactor 2 is scrubbed in a scrubbing contactor 6 with a scrub solution 7 containing manganese and copper. Scrubbed loaded organic solution 8 is selectively stripped with a first acid, a dilute sulphuric acid 9, in a stripping contactor 10 to form scrub solution 7, part of which is recycled to scrubbing contactor 6. Partially stripped organic extractant 11 is then stripped of all impurities with a second acid, dilute hydrochloric acid 12, in a bulk stripping contactor 13. Stripped organic solution 3 is recycled to extraction contactor 2.

Two alternative flow charts resulting from preferred embodiments of the invention are shown in Figures 2 and 3. Figure 2 shows a flow chart in which the organophosphoric acid is used in the first solvent extraction stage and the organophosphinic acid is used in the second solvent extraction stage. Figure 3 shows the reverse situation in which the organophosphinic acid is used in the first solvent extraction phase and the

organophosphoric acid is used in the second solvent extraction stage.

A preferred embodiment of the invention is described with reference to the accompanying example.

#### EXAMPLE 1

Separation of nickel and cobalt from manganese and other impurities, using a synthetic nickel laterite acid leach solution.

##### A. Hydroxide precipitation

Magnesia is added to the aqueous leach liquor to precipitate out target elements cobalt and nickel as hydroxides, leaving behind the impurities magnesium and calcium (and some manganese) in the liquid phase. Following the precipitation step, the solid liquid separation and re-leaching in sulphuric acid, the leach solution has the composition set out in Table 1.

Table 1 Composition of typical acid leach solution

Elements	Concentration (g/L)	
	Before PPN with MgO	After acid Leaching
Ni	3.0	60.0
Co	0.3	3.0
Cu	0.1	1.0
Zn	0.1	1.0
Ca	0.5	0.1
Mn	2.0	1.0
Mg	3.0	0.1

NB Precipitate leached with acid containing 30g/l Ni (see Figures 2 and 3)

1. Extraction with an organophosphoric acid-containing organic solution.

The aim of the extraction is to extract all the zinc, copper and manganese (and calcium, to the extent that it is still present) from the aqueous leach solution ("PLS"

- plant leach solution) into the organophosphoric acid-containing solution and to minimise the extraction of cobalt (and nickel and magnesium, to the extent that they are present). This step is described in further detail below with reference to a leaching step conducted on a synthetic iron-free laterite leach solution containing 2.60 g/L Ni, 0.24 g/L Co, 0.27 g/L Zn, 0.52 g/L Ca, 0.09 g/L Cu, 1.87 g/L Mn and 2.89 g/L Mg.

10                   The organic solution consisted of 12% di-2-ethylhexyl phosphoric acid (D2EHPA), 2.5% tri-n-butyl phosphate (TBP) and 85.5% kerosene (Shellsol 2046), all by volume. Four counter-current extraction stages were used at an A/O flowrate ratio of 1:1. The pH in the four mixers was  
15                   controlled at 3.7 using three pH controllers with the addition of ammonia solution (Fig 1). The results are shown in Table 1. All the zinc, calcium, manganese and copper were extracted in four stages. Some 12.6% cobalt, 20% magnesium and no nickel were co-extracted. The raffinate  
20                   contained only cobalt, nickel and magnesium.

                  If the D2EHPA extraction described above had been preceded by the magnesia precipitation step described above, Mg (and Ca) would already have been removed (Figs 2  
25                   and 3), leaving only Co and Ni in the raffinate (Fig 2). The Ni/Co raffinate could then proceed to a subsequent solvent extraction step where cobalt would be extracted from the aqueous solution by di-2, 4, 4-trimethylpentyl phosphinic acid (Cyanex 272), using a well known and proven  
30                   commercial process. The cobalt and nickel could be then recovered by electrowinning from the Cyanex strip and raffinate solutions respectively (Fig 2), again using the known technology.

35                   Alternatively, if the D2EHPA extraction described above had been preceded by the known magnesia precipitation step described above, and a known Cyanex 272 extraction, Ni

and Mg (and Ca) would already have been removed, leaving only Co in the D2EHPA raffinate, which could be recovered by hydroxide precipitation (Fig 3). Ni could be recovered by electrowinning from the Cyanex raffinate.

5

In both flowsheet configurations, the nickel electrowinning spent electrolyte containing sulfuric acid is recycled to the hydroxide precipitate releach (Figs 2 and 3).

10

Table 2 Summary of semi-continuous extraction test results

Metal name	Concentration (g/L)			Total extraction (%)
	In feed	In loaded organic	In raffinate	
Zn	0.265	0.255	0.000	100.00
Ca	0.516	0.605	0.000	100.00
Mn	1.865	1.775	0.000	100.00
Cu	0.094	0.089	0.000	100.00
Co	0.240	0.031	0.196	12.57
Ni	2.597	0.000	2.535	0.000
Mg	2.893	0.590	2.130	20.12

## 2. Scrubbing

15

The aim of scrubbing is to scrub all of the co-extracted cobalt (and nickel, if present) and also magnesium if present, from the D2EHPA organic extraction solution to the aqueous scrub raffinate and to minimise the scrubbing of manganese, copper, calcium and zinc.

20

25

Two scrubbing stages were used with a combined solution of manganese (6.78 g/L) and copper (0.35 g/L) at an A/O flowrate ratio of 1:5. Scrubbing results are listed in Table 3. The cobalt and nickel scrubbing efficiencies were 100% with no cobalt and nickel being left in the organic solution. This scrub raffinate containing 0.142 g/L

cobalt is recycled back to the feed. By doing this, the cobalt and nickel recovery approaches 100%.

Table 3 Summary of scrubbing test results using a combined  
5 Mn and Cu scrub solution

Metal name	Concentration (g/L)				Total scrub efficiency (%)
	Scrub solution	loaded organic	scrubbed organic	scrub raffinate	
Zn	0.000	0.255	0.256	0.000	0.00
Ca	0.035	0.605	0.610	0.054	-0.82
Mn	6.781	1.775	3.095	0.926	-41.65
Cu	0.349	0.089	0.146	0.112	-35.45
Co	0.000	0.031	0.000	0.142	100.00
Ni	0.000	0.000	0.000	0.001	100.00
Mg	0.019	0.590	0.000	2.372	100.00

### 3. Selective stripping

The aim of selective stripping is to generate a  
10 solution containing mainly manganese and copper for using as scrubbing solution in the previous stage.

One selective strip stage was used at an A/O  
flowrate ratio of 1:5 with 14.9 g/L sulphuric acid. The  
15 results are shown in Table 4. The strip raffinate contained 7.3 g/L manganese and 0.54 g/L copper, which was just slightly higher than the scrubbing solution used in the previous stage (6.78 g/L manganese and 0.35 g/L copper). However this could be easily corrected by using slightly  
20 more dilute sulphuric acid for stripping, say 12 g/L.

### 4. Bulk stripping

The aim of bulk stripping is to re-generate the organic D2EHPA solution by stripping all elements from the  
25 organic extractant.

Two bulk strip stages were used at an A/O flowrate ratio of 1:5 with 37 g/L hydrochloric acid. The results are also shown in Table 4. All the zinc, calcium, copper and manganese were stripped. If no calcium is present in the feed (which is the case when the preliminary precipitation step has been conducted), sulphuric acid can be used for bulk stripping.

Table 4 Summary of semi-continuous stripping test results with an A/O ratio of 1:5

Metal name	Concentration (g/L)			Total strip efficiency (%)
	Scrubbed organic	Stripped organic 1	Strip raffinate 1	
(Selective strip, 14.9 g/L H <sub>2</sub> SO <sub>4</sub> )				
Zn	0.256	0.255	0.022	1.73
Ca	0.610	0.405	0.280	33.28
Mn	3.095	1.570	7.319	46.78
Cu	0.146	0.030	0.540	78.26
(Bulk strip, 36.6 g/L HCl)				
	Stripped organic 1	Stripped organic 2	Strip raffinate 2	
Zn	0.255	0.000	1.494	100.00
Ca	0.405	0.000	2.401	100.00
Mn	1.570	0.000	8.679	100.00
Cu	0.030	0.000	0.159	100.00

It will be understood to persons skilled in the art of the invention that various modifications could be made to the preferred embodiments illustrated and described above without departing from the spirit and scope of the invention.

## CLAIMS:

1. A method of separating cobalt and nickel from other elements contained in an aqueous leach solution, the method including the steps of:
- 5 (a) adding a precipitating agent to the aqueous leach solution to precipitate elements including cobalt and nickel;
- 10 (b) separating the precipitate from the treated aqueous leach solution;
- (c) leaching the precipitate with an acid to form a leach liquor; and
- (e) 15 subjecting the leach liquor to successive solvent extraction steps with an organophosphoric acid and an organophosphinic acid.
2. The method as claimed in claim 1, wherein the precipitate is a hydroxide, a carbonate or an oxylate salt.
- 20 3. The method as claimed in claim 1 or claim 2, wherein the acid used in step (c) is selected from the group consisting of sulphuric acid, hydrochloric acid and nitric acid.
- 25 4. The method as claimed in any one of the preceding claims, wherein the precipitation step effects the removal of magnesium and calcium (to the extent that these elements are present in the aqueous leach solution), and some manganese, which elements remain in the aqueous leach
- 30 solution.
5. The method as claimed in any one of the preceding claims, wherein the process includes the further step of recovering nickel from the raffinate of the
- 35 organophosphinic acid solvent extraction step.
6. The method as claimed in claim 5, wherein the



nickel is recovered by electrowinning.

7. The method as claimed in claim 6, wherein spent electrolyte from the nickel electrowinning step is recycled to the leach step (c).

8. The method as claimed in any one of the preceding claims, wherein the organophosphoric acid is of the formula  $(RO)_2PO_2H$ , in which each R group, which may be the same or different, is an optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl group.

9. The method as claimed in claim 8, wherein each R group has a minimum of 4 carbon atoms.

10. The method as claimed in claim 8, wherein each R group has between 6 to 18 carbon atoms.

11. The method as claimed in claim 8, wherein R is n-octyl, cyclooctyl or 2-ethylhexyl.

12. The method as claimed in any one of claims 1 to 7, wherein the organophosphoric acid is di-2-ethylhexyl phosphoric acid, or an organophosphoric acid having extraction characteristics similar to or the same as di-2-ethylhexyl phosphoric acid.

13. The method as claimed in any one of the preceding claims, wherein the organophosphinic acid is of the formula  $R_2PO_2H$ , in which the two R groups, which may be the same or different, are selected from optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl groups.

14. The method as claimed in claim 13, wherein the two R groups each contain a minimum of 4 carbon atoms.

15.           The method as claimed in claim 13, wherein the two R groups each contain from 6 to 18 carbon atoms.

16.           The method as claimed in any one of claims 1 to  
5 12, wherein the organophosphinic acid is di-2,4,4-trimethylpentyl phosphinic acid or an organophosphinic acid having extraction characteristics similar to or the same as di-2,4,4-trimethylpentyl phosphinic acid.

10 17.           The method as claimed in any one of the preceding claims, wherein a modifier is used in the organophosphoric and organophosphinic acid solvent extraction stages to facilitate phase separation of the aqueous and organic phases.

15 18.           The method as claimed in claim 17, wherein the modifier is tri *n*-butyl phosphate.

19.           The method as claimed in any one of the preceding  
20 claims, wherein the organic solvent used in the organophosphoric and organophosphinic acid solvent extraction stages is kerosene.

20.           The method as claimed in any one of the preceding  
25 claims, wherein the leach liquor obtained following the leach step (c) is subjected to solvent extraction with organophosphoric acid, after which the aqueous raffinate from the organophosphoric acid leaching stage is subjected to solvent extraction with the organophosphinic acid,  
30 nickel is recovered from the organic raffinate of the organophosphinic solvent extraction step and cobalt is recovered from the aqueous strip liquor.

21.           The method as claimed in claim 20, wherein the  
35 cobalt is recovered from the aqueous strip liquor by electrowinning, and spent electrolyte from the cobalt electrowinning step is recycled to the organophosphinic

acid extraction step.

22. The method as claimed in any one of claims 1 to 19, wherein the leach liquor obtained following the leach  
5 step (c) is subjected to solvent extraction with organophosphinic acid, nickel is recovered from the raffinate of the organophosphinic acid extraction stage, and the aqueous strip liquor from the organophosphinic acid extraction stage is subjected to solvent extraction with  
10 organophosphoric acid to produce a raffinate from which cobalt is recovered.

23. The method as claimed in claim 22, wherein the  
15 cobalt recovered by precipitation.

24. The method as claimed in any one of the preceding claims, wherein the loaded organic phase resulting from solvent extraction with organophosphoric acid is scrubbed with an aqueous scrub solution containing manganese and  
20 copper, which aqueous scrub solution is obtained by conducting a selective strip on a scrubbed loaded organic solution produced in the scrubbing step, and recycling the manganese and copper-containing aqueous solution back to the scrubbing stage to be used as the aqueous scrub  
25 solution.

25. The method as claimed in claim 24, wherein a spent aqueous scrub solution generated in the scrubbing step is then recycled to the leach solution of the  
30 organophosphoric acid extraction step to maximise the recovery of cobalt (and nickel, if present), and the selectively stripped organic solution is subjected to bulk stripping to remove a large proportion of the cations remaining therein to be recycled for use as the organic  
35 phase in the initial extraction step.

26. The method as claimed in any one of claims 1 to

19, wherein the organophosphoric acid extraction step is conducted prior to the organophosphinic acid extraction step, and the organophosphoric acid extraction step involves:

- 5 I. contacting the leach liquor produced in step (c) with an organic solution comprising an organophosphoric acid and a modifier dissolved in an organic solvent to produce a loaded organic solution containing manganese and, to the extent that they are present, zinc and  
10 copper, and a some cobalt and nickel, and an aqueous raffinate solution containing most of the cobalt and nickel;
  - II. scrubbing the loaded organic solution with an aqueous scrub solution containing manganese and copper to  
15 produce a scrubbed organic solution containing less cobalt and nickel and a spent aqueous scrub solution containing some cobalt and nickel, as well as manganese;
  - III. recycling the spent aqueous scrub solution to step I;  
20 and
  - IV. selectively stripping the scrubbed organic solution to remove a portion of the manganese and copper to form the aqueous scrub solution for use in step II.
- 25 27. The method as claimed in any one of claims 1 to 19, wherein the organophosphoric acid extraction step is conducted following the organophosphinic acid extraction step, and the organophosphoric acid extraction step involves:
- 30 I. contacting the aqueous strip liquor from the organophosphinic acid extraction stage with an organic solution comprising an organophosphoric acid and a modifier dissolved in an organic solvent to produce a loaded organic solution containing manganese and, to  
35 the extent that they are present, zinc and copper, and a some cobalt, and an aqueous raffinate solution containing most of the cobalt;

- II. scrubbing the loaded organic solution with an aqueous scrub solution containing manganese and copper to produce a scrubbed organic solution containing less cobalt and a spent aqueous scrub solution containing some cobalt, as well as manganese;
- 5 III. recycling the spent aqueous scrub solution to step I; and
- IV. selectively stripping the scrubbed organic solution to remove a portion of the manganese and copper to form
- 10 the aqueous scrub solution for use in step II.

28. The method as claimed in claim 26 or claim 27, wherein the scrubbed organic solution is selectively stripped of manganese and copper by contacting the scrubbed

15 organic solution with an acid.

29. The method as claimed in claim 28, wherein the acid is sulphuric acid.

20 30. The method as claimed in claim 28 or claim 29, wherein the selective stripping stage yields a selectively stripped organic solution, and the selectively stripped organic solution is bulk stripped of cations by contacting the selectively stripped organic solution with a second

25 acid, and the bulk stripped organic solution is recycled to step I.

31. The method as claimed in claim 30, wherein the second acid is hydrochloric acid.

30 32. The method as claimed in any one of claims 26 to 30, wherein the mole ratio of  $(\text{Mn}+\text{Cu})/(\text{Co}+\text{Ni})$  in the aqueous scrub solution is at least 1.5.

33. The method as claimed in any one of the preceding

35 claims, wherein the method does not include a sulphide precipitation stage for separating cobalt from manganese.

34. A plant for separating cobalt and nickel from impurities contained in a leach solution as defined in claim 26, the plant including:

- 5       - a precipitation tank in which the aqueous leach solution is contacted with a precipitating agent;
- a solid liquid separator (such as a thickener) in which the aqueous leach liquor following the precipitation step is separated from the precipitate;
- 10       - a re-leaching tank in which the precipitate is re-leached;
- an organophosphoric acid solvent extraction contactor in which the re-leached liquor is contacted with the organophosphoric acid-containing organic solution;
- a scrubbing contactor for scrubbing the loaded organic  
15       solution generated in solvent extraction contactor;
- a stripping contactor in which the scrubbed organic solution generated in the scrubbing contactor is subjected to selective stripping to generate the aqueous scrub solution for use in the scrubbing contactor;
- 20       - a scrubbed organic solution conduit for conducting the scrubbed organic solution to the stripping contactor;
- an aqueous scrub solution conduit for conducting the aqueous scrub solution from the stripping contactor to the scrubbing contactor;
- 25       - a spent aqueous scrub solution conduit for conducting the spent aqueous scrub solution from the scrubbing contactor to the solvent extraction contactor; and
- an organophosphinic acid solvent extraction circuit in which the aqueous raffinate solution generated in the  
30       organophosphoric acid solvent extraction contactor is extracted with an organophosphinic acid.

35. A plant for conducting the method as claimed in claim 27, the plant including:

- 35       - a precipitation tank in which the aqueous leach solution is contacted with a precipitating agent;
- a solid liquid separator (such as a thickener) in which

- the aqueous leach liquor following the precipitation step is separated from the precipitate;
- a re-leaching tank in which the precipitate is re-leached;
  - 5 - an organophosphinic acid solvent extraction circuit in which the re-leached liquor generated in the re-leaching tank is extracted with an organophosphinic acid;
  - an organophosphoric acid solvent extraction contactor in which the aqueous strip liquor from the organophosphinic acid solvent extraction circuit is contacted with the
  - 10 organophosphoric acid-containing organic solution;
  - a scrubbing contactor for scrubbing the loaded organic solution generated in solvent extraction contactor;
  - a stripping contactor in which the scrubbed organic
  - 15 solution generated in the scrubbing contactor is subjected to selective stripping to generate the aqueous scrub solution for use in the scrubbing contactor;
  - a scrubbed organic solution conduit for conducting the scrubbed organic solution to the stripping contactor;
  - 20 - an aqueous scrub solution conduit for conducting the aqueous scrub solution from the stripping contactor to the scrubbing contactor; and
  - a spent aqueous scrub solution conduit for conducting the spent aqueous scrub solution from the scrubbing
  - 25 contactor to the solvent extraction contactor.

36. The plant as claimed in claim 35, wherein the plant further includes an organic solution recycle conduit for conducting the partially stripped scrubbed solution

30 from the stripping contactor to the organophosphoric acid solvent extraction contactor.

37. The plant as claimed in claim 36, wherein a bulk stripping contactor is located in the recycle conduit, in

35 which the partially stripped scrubbed solution is stripped of remaining impurities before being conducted to the solvent extraction contactor.

38. The plant as claimed in any one of claims 35 to 37, wherein the solvent extraction contactors are a countercurrent solvent extraction contactor.

5

39. The plant as claimed in any one of claims 35 to 38, wherein the plant also includes an electrolytic cell for the recovery of nickel, and either a cobalt electrolytic cell or a cobalt precipitation tank.

10



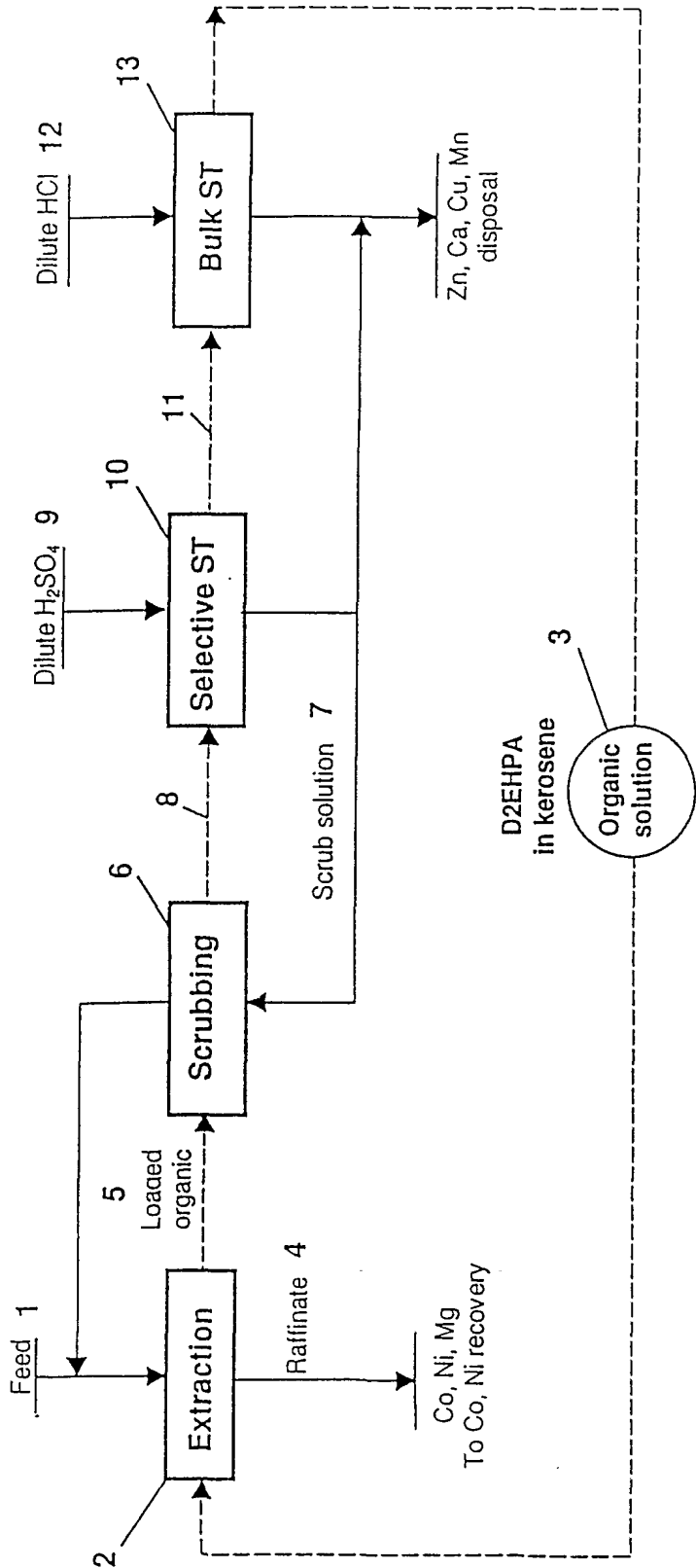


FIGURE 1

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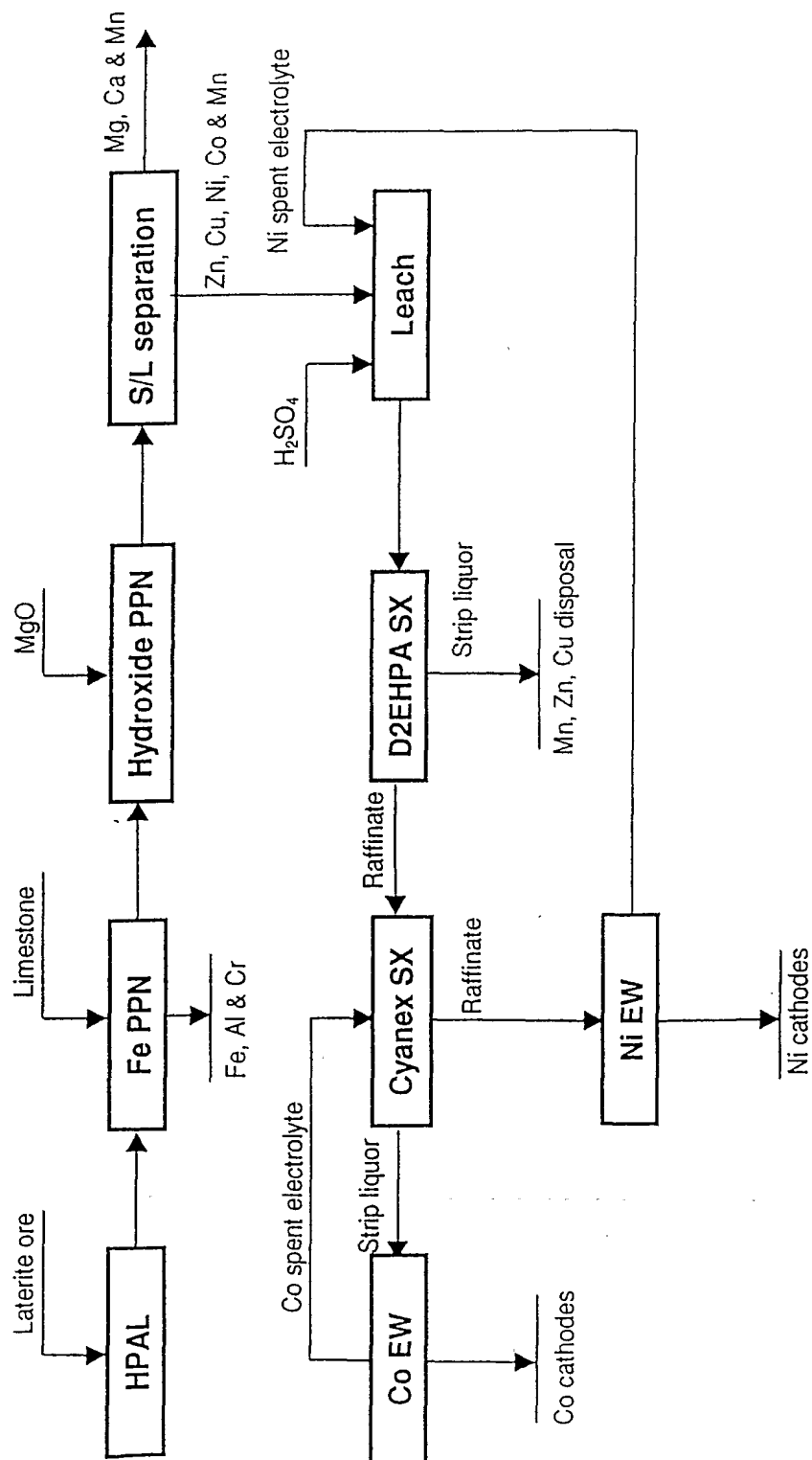


FIGURE 2

3 / 3

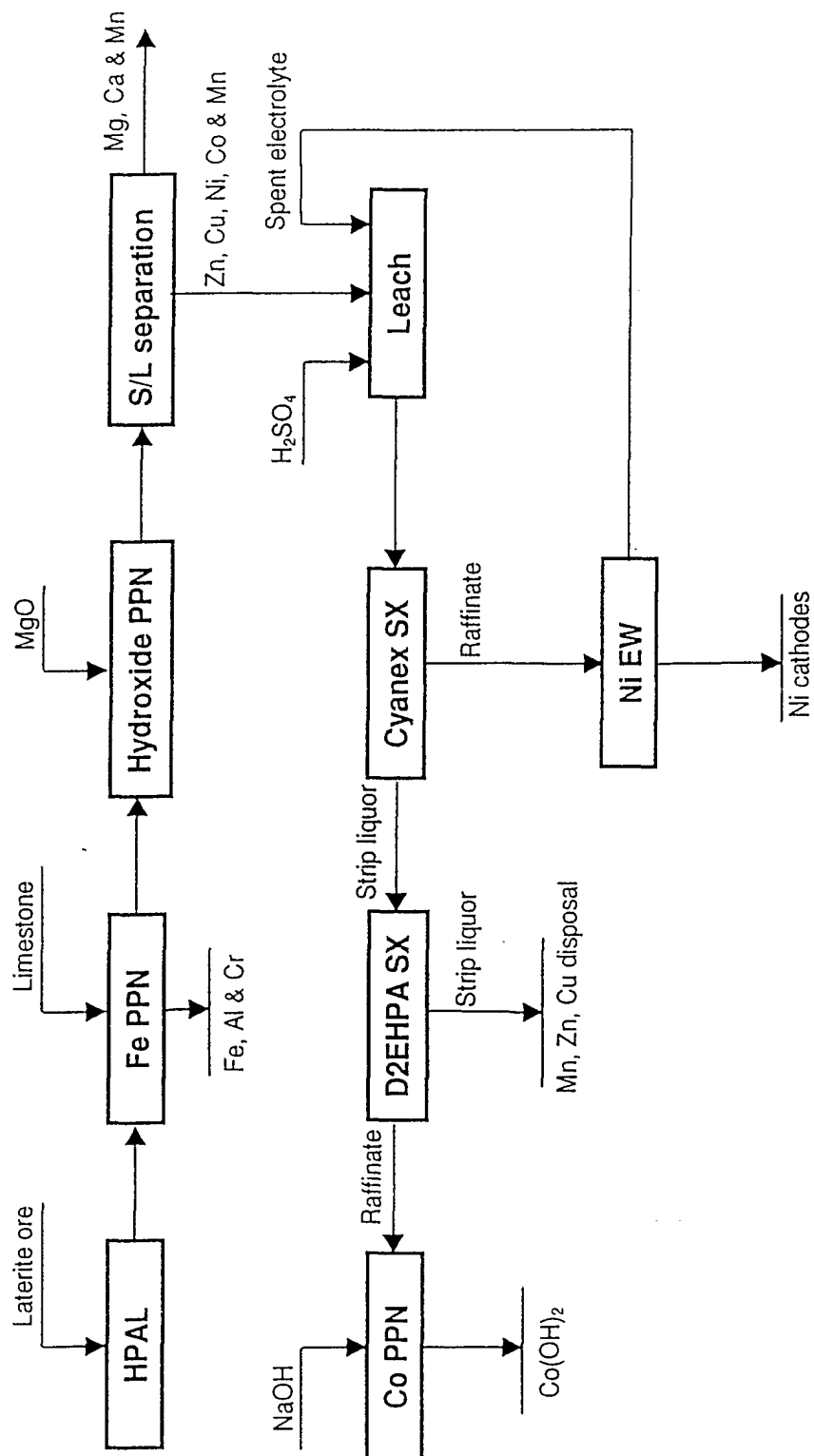


FIGURE 3

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/AU01/01162****A. CLASSIFICATION OF SUBJECT MATTER**Int. Cl. <sup>7</sup>: C22B 3/26, 3/38, 23/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC<sup>7</sup> AS ABOVE

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched


Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Derwent WPAT: IPC<sup>7</sup> as above and Cobalt or Nickel or Solvent or Extract+**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AU 40890/96 A (Resolute Resources Ltd) 18 July 1996 Whole Document	
A	US 5447552 A (Mihaylov et al) 5 September 1995 Whole Document	
A	US 5378262 A (Mihaylov et al) 3 January 1995 Whole Document	
A	EP 210387 A1 (American Cyanamid Co) 4 February 1987 Whole Document	

☐ Further documents are listed in the continuation of Box C
 ☒ See patent family annex

* Special categories of cited documents:	
"A" Document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
8 November 2001Date of mailing of the international search report  
13 NOV 2001Name and mailing address of the ISA/AU  
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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/AU01/01162**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member				
AU	40890/96	NONE					
US	5447552	AU	14966/95	BR	9501135	CA	2145054
		CN	1109913	FR	2717826	JP	8035023
		OA	10135	US	5378262	ZA	9502338
EP	210387	AU	60454/86	BR	8603438	FI	863027
		JP	62027529	US	4721605	ZA	8605499
END OF ANNEX							